

## Spotlights on Recent JACS Publications

### ■ PROGRESS TOWARD IMPROVED UP- AND DOWN-CONVERSION MATERIALS

When photons are captured by light-harvesting materials, such as in a solar cell or other photovoltaic device, photons that have a lower energy than the band gap of the material are lost. The process of up- or down-conversion can improve energy harvesting over a broader spectrum of light by either converting multiple low-energy photons into a photon with higher energy, or the opposite. Alkali–rare earth metal fluorides (AREFs) have been well-established as some of the most effective conversion materials. But many of the methods for creating AREFs utilize high pressure and temperature and long reaction times, which can adversely impact the properties of the final product.

Now, researchers led by Evgeny Dikarev report a class of alkali–rare earth metal coordination compounds that can be created in a large-scale, high-yielding one-pot reaction with commonly available starting reagents at a low temperature (DOI: [10.1021/jacs.6b04194](https://doi.org/10.1021/jacs.6b04194)). The approach involves a single-source fluorinated  $\beta$ -diketonate precursor, which allows researchers better control over material stoichiometry at the molecular level. The result is a heterometallic precursor with desirable properties—high volatility, an optimal 1:1 metal ratio, and reasonable stability in open air—and these new compounds could be applied in the improved preparation of light-harvesting AREF materials.

Christine Herman, Ph.D.

### ■ HYDROGEN EVOLUTION FROM A BIMETALLIC ENZYME

Sharon Hammes-Schiffer, Thomas Rauchfuss, and colleagues have determined the mechanism by which an analogue of nickel–iron hydrogenase evolves hydrogen through experimental and computational study of a synthetic mimic of the enzyme's active site (DOI: [10.1021/jacs.6b04579](https://doi.org/10.1021/jacs.6b04579)).

Hydrogenases catalyze the reversible reduction of protons to generate hydrogen. They are promising tools in efforts to make hydrogen fuel, and they also have applications in industrial catalysis. Researchers want to understand the mechanism of these natural enzymes, including the [NiFe] hydrogenases, in order to replicate their chemistry with synthetic versions and potentially adapt them for a variety of uses.

Working toward this goal, the authors have studied the active site of a [NiFe] hydrogenase analogue through NMR and EPR spectroscopy, X-ray crystallography, and density functional theory. They find that the behavior of the catalyst depends on a specific interaction between the two parts of the bimetallic unit of the active site. Reduction at the nickel center yields a nickel–iron hydride, which is a critical intermediate in the mechanism of hydrogen evolution. When the iron hydride is then protonated, hydrogen is released.

Deirdre Lockwood, Ph.D.

### ■ FEMTOSECOND SPECTROSCOPY REVEALS METALLOPORPHYRIN CHARGE TRANSFER

Metalloporphyrins have been investigated for their potential application as photocatalysts, light sensitizers, and electron donors and acceptors. Upon excitation with light, they respond with extremely fast charge-transfer processes that reinforce interest in these compounds for photochemical applications.

Charge-transfer processes in complex molecules have been studied over the past 15 years by X-ray transient absorption spectroscopy using X-ray pulses from synchrotron sources with  $\sim 100$  ps durations. In the case of visualizing electron transfer of the initial excited states of metalloporphyrins with open-shell metal centers, however, the synchrotron X-ray pulse duration is too long. A first femtosecond hard X-ray source—the Linac Coherent Light Source—came online in 2009 at the SLAC National Accelerator Laboratory in Menlo Park, CA, and has brought the study of ultrafast electron transfer within reach.

Now, Lin X. Chen, Xiaosong Li, Brian M. Hoffman, and co-workers report the observation of a transient nickel(I) porphyrin species, lasting slightly longer than a picosecond, resulting from the intramolecular electron transfer caused by relaxation following the initial excitation of nickel(II) tetramesitylporphyrin (DOI: [10.1021/jacs.6b02176](https://doi.org/10.1021/jacs.6b02176)). The researchers go on to verify the nickel species with time-dependent density functional theory methods. Identifying intermediates of potential photocatalytic significance will facilitate the fine-tuning and optimization of organometallic photoactive molecules incorporating different metals and ligands.

Alexander Helleman

### ■ COPPER–PORPHYRIN CATALYST CONVERTS CARBON DIOXIDE TO HYDROCARBONS

To produce fuel in a sustainable manner, chemists look to the development of new electrocatalysts that use renewable energy to convert carbon dioxide to hydrocarbons. This type of conversion reaction, however, requires a large amount of energy because  $\text{CO}_2$  is relatively stable and inert, and multiple electrons must be transferred during the reduction.

To reduce the energy needed for this reaction, Gary Brudvig, Hailiang Wang, and their colleagues have made an improved catalyst electrode by depositing copper–porphyrin molecules onto carbon fiber paper (DOI: [10.1021/jacs.6b04746](https://doi.org/10.1021/jacs.6b04746)). In an aqueous solution saturated with  $\text{CO}_2$  at  $-0.976$  V (versus the reversible hydrogen electrode), the catalyst-covered electrode mainly reduces  $\text{CO}_2$  to methane and ethylene. In contrast, some similar organometallic electrocatalysts work in organic solvents and produce oxygenated products like carbon monoxide.

The oxidation state of the copper ion and the hydroxyl groups on the porphyrin pointing toward the center of the complex are important factors in producing hydrocarbons instead of oxygenated products, suggesting to the researchers that catalysts like this could be designed and tailored for  $\text{CO}_2$  reduction.

Melissae Fellet, Ph.D.

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